

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>A23D 9/00, C11C 3/12</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/17667</b> <b>(43) International Publication Date:</b> 28 November 1991 (28.11.91)
<b>(21) International Application Number:</b> PCT/US91/02685 <b>(22) International Filing Date:</b> 22 April 1991 (22.04.91) <b>(30) Priority data:</b> 523,088 14 May 1990 (14.05.90) US <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventor:</b> PURVES, Edward, Robert ; 11725 Hollingsworth Way, Forest Park, OH 45240 (US). <b>(74) Agents:</b> REED, T., David; The Procter & Gamble Com- pany, Ivorydale Technical Ctr., 5299 Spring Grove Ave., Cincinnati, OH 45217-1087 (US) et al.		<b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European pa- tent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (Euro- pean patent), IT (European patent), LU (European pa- tent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HYDROGENATED FRYING FAT WITH EXTENDED FRYLIFE  <b>(57) Abstract</b>  A hydrogenated frying fat with extended frylife is made by: (a) hydrogenating an edible liquid oil having a starting iodine value between 95 and 150 by reacting the liquid oil with hydrogen in the presence of 0.01 % to 0.4 % hydrogenation catalyst by weight of the oil, where the hydrogenation reaction is conducted at a temperature between 320 °F (160 °C) and 500 °F (260 °C) and a pressure between 0 psig and 100 psig until the iodine value of the oil after hydrogenation is between 50 and 90, and where during the hydrogenation reaction the temperature of the oil is between 440 °F (227 °C) and 500 °F (260 °C) for a time of at least 5 minutes and until the desired endpoint is reached; then (b) cooling the oil, filtering the oil to remove the catalyst, storing the oil at a temperature of 110 °F (43 °C) to 220 °F (104 °C), and deaerating the oil; and then (c) deodorizing the oil by heating it at a temperature between 530 °F (277 °C) and 650 °F (343 °C), at a pressure between 0.5 mm Hg and 50 mm Hg, for a time between 5 seconds and 35 minutes, while stripping the oil with a stripping medium in the amount of 0.1 % to 20 % by weight of the oil.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

-1-

## HYDROGENATED FRYING FAT WITH EXTENDED FRYLIFE

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to hydrogenated frying fats and to a method for making the fats by high temperature hydrogenation and deodorization.

2. Description of the Related Art

U.S. Patent 4,789,554 to Scavone et al., issued December 6, 1988, discloses a high temperature deodorization process used to purify and increase the frylife of edible oils. Deaerated oil is deodorized at a temperature between 530°F (277°C) and 650°F (343°C) for a time between 5 seconds and 15 minutes. Tocopherols and related structures believed to be deleterious to frylife are removed. The patent does not discuss hydrogenation.

U.S. Patent 2,602,806 to Jacob, Jr., et al., issued July 8, 1952, discloses a hydrogenation process for triglycerides in which the hydrogenation is conducted at temperatures up to 545°F (285°C).

U.S. Patent 2,621,191 to Thurman, issued December 9, 1952, discloses a deodorization process for glyceride oils conducted at temperatures between 500°F (260°C) and 600°F (316°C). Hydrogenation of the oils is done at a temperature of about 400°F or less.

U.S. Patent 3,732,266 to Dudrow, issued May 8, 1973, discloses a method for hydrogenating oils at a temperature between about 240°F (116°C) and about 450°F (232°C).

U.S. Patent 4,260,643 to Cochran, issued April 7, 1981, discloses triglycerides hydrogenated by a two-step process, where the first hydrogenation step is carried out at

-2-

325°F-460°F (163°C-238°C) and the second hydrogenation step is carried out at 340°F-460°F (171°C-238°C).

U.S. Patent 3,555,058 to Going et al., issued January 12, 1971, discloses a special catalytic hydrogenation process. The temperature of reaction is said to vary between about 150°F (66°C) and about 500°F (260°C).

The above-mentioned Scavone et al. '554 patent discloses a method for increasing the frylife of edible oils by deodorizing the oils at high temperatures between 530°F (277°C) and 650°F (343°C) and under other specified conditions. However, the Scavone et al. patent does not teach or suggest that a particular high temperature hydrogenation process used in combination with the deodorization process can have an additional effect in improving frylife.

Other of the above-mentioned patents disclose hydrogenation processes carried out at high temperatures. However, the patents do not suggest that the method of hydrogenation can affect the frylife of edible fats. Moreover, the patents do not suggest that the optimum frylife can be obtained in fats by processing the fats in a high temperature deodorization process combined with a high temperature hydrogenation process.

It is, therefore, an object of the present invention to provide a method for improving the frylife of edible fats by use of a specific high temperature deodorization process in combination with a specific high temperature hydrogenation process.

It is another object of the present invention to provide the hydrogenated fats that have improved frylife, and that are characterized by low levels of tocopherols and high levels of *trans*-isomers.

These and other objects of the invention will become evident from the disclosure herein.

All parts, percentages and ratios used herein are by weight unless otherwise defined.

**SUBSTITUTE SHEET**

-3-

SUMMARY OF THE INVENTION

The invention is a process for making a hydrogenated frying fat with extended frylife comprising:

- a) hydrogenating an edible liquid oil having a starting iodine value between about 95 and about 150 by reacting the liquid oil with hydrogen in the presence of about 0.01% to about 0.4% hydrogenation catalyst by weight of the oil, wherein the hydrogenation reaction is conducted at a temperature between about 320°F (160°C) and about 500°F (260°C) and a pressure between about 0 psig and about 100 psig until the iodine value of the oil after hydrogenation is between about 50 and about 90, and wherein during the hydrogenation reaction the temperature of the oil is between about 440°F (227°C) and about 500°F (260°C) for a time of at least about 5 minutes and until the desired endpoint is reached; then
- b) cooling the oil, filtering the oil to remove the catalyst, storing the oil at a temperature of about 110°F (43°C) to about 220°F (104°C), and deaerating the oil; and then
- c) deodorizing the oil by heating it at a temperature between about 530°F (277°C) and about 650°F (343°C), at a pressure between about 0.5 mm Hg and about 50 mm Hg, for a time between about 5 seconds and about 35 minutes, while stripping the oil with a stripping medium in the amount of about 0.1% to about 20% by weight of the oil.

The present invention also relates to a hydrogenated frying fat with extended frylife, wherein the hydrogenated fat has an iodine value between about 50 and about 90, and wherein the hydrogenated fat contains at least about 35% *trans*-isomers.

-4-

DESCRIPTION OF THE PREFERRED EMBODIMENTS1. Discovery of Frylife Benefit from Hydrogenation

It has now been discovered that a high temperature hydrogenation process can increase the frylife of an edible frying fat. Moreover, when the high temperature hydrogenation process described herein is combined with a particular high temperature deodorization process, it has been discovered that the frylife of the resulting frying fat is improved over that of a fat undergoing the high temperature deodorization process alone. Although not intending to be bound by theory, it is believed that a higher level of *trans*-isomers in the frying fat, which results from the high temperature hydrogenation process, is involved in the improved frylife benefit of the invention.

2. Hydrogenation

Hydrogenation is a means of saturating oils by the addition of hydrogen to the double bonds (unsaturated or ethylenic bonds) of an oil or fat by reaction with hydrogen in the presence of a metal catalyst. The hydrogenation reaction is accompanied by the simultaneous isomerization, both positional and geometrical, of the unsaturated bonds, producing both *trans*-isomers and *cis*-isomers.

Both Swern, *Bailey's Industrial Oil and Fat Products*, 3rd ed., 1964, pp. 305-313 and 793-886, and Swern, *Bailey's Industrial Oil and Fat Products*, Vol. 2, 4th ed., 1982, pp. 5-69, discuss the hydrogenation process in general. Beckmann, "Hydrogenation Practice", *JAOCs*, Vol. 60, No. 2, February 1983, pp. 282-290, discusses hydrogenation practice, equipment, process controls, and catalysts.

For hydrogenation to take place, gaseous hydrogen, liquid oil, and the solid catalyst must be brought together at a suitable temperature. In the usual type of equipment, a suspension of catalyst and oil is agitated in a closed vessel in an atmosphere of hydrogen.

SUBSTITUTE SHEET

-5-

Hydrogenation, like other chemical reactions, is accelerated by an increase in temperature or pressure. Also, as the temperature of reaction is increased, the formation of *trans* unsaturation increases almost linearly. The effect of pressure on isomerization is limited, and the rate of increase in the formation of *trans* isomers is less at higher pressures.

Commercial hydrogenation plants are essentially divided between "recirculation" systems, in which agitation and dispersion of hydrogen within the oil are achieved by continuously recycling hydrogen in large volumes through the reactor, and the newer "dead-end" systems in which the reactor is supplied only with as much hydrogen as is absorbed, and where dispersion of the hydrogen is assisted by mechanical agitation. Any type of commercially acceptable processing operation, including batch hydrogenation, continuous processing, recirculation systems, and "dead-end" systems, may be utilized with the hydrogenation process described herein. For a thorough discussion of hydrogenation equipment, see Swern, *Bailey's Industrial Oil and Fat Products*, Vol. 2, 4th ed., 1982, pp. 27-37.

The starting oil for the hydrogenation process of the present invention can be any edible liquid vegetable, animal or marine oil or blend of oils which has an iodine value of from about 95 to about 150. The preferred oil is a polyunsaturated vegetable oil having fatty acid chains containing at least 14 carbon atoms. Preferred vegetable oils include soybean, corn, cottonseed, sunflower seed, safflower, olive, peanut, coconut, palm, rapeseed, palm oil olein, and canola oil. More preferred oils include soybean, sunflower seed, palm oil, peanut oil, canola oil, corn oil, cottonseed oil, safflower oil, and mixtures thereof. The most preferred oils are soybean oil and canola oil, and mixtures thereof.

A blend of two or more oils may be used to obtain the desired initial iodine values and the desired stability in

-6-

the oil after hydrogenation. The oils may be blended either prior to or following hydrogenation. Oils with high iodine values, such as liquid soybean oil, are useful in limited amounts when blended with oils that have been hydrogenated to control the consistency and solids content of the final product.

The oil is mixed with any conventional hydrogenation catalyst known to the hydrogenation industry. Finely divided metallic nickel catalysts are well known for use in the hydrogenation of vegetable oils. Such catalysts are usually deposited on carriers such as Kieselguhr, aluminum oxide, silicate and the like.

Nickel catalysts can lose their activity, or be deactivated, due to the poisoning action of certain chemical substances, such as sulfur, phosphorus, chlorine, zinc, and compounds of the same. For the hydrogenation process of the present invention, it is preferred to use a nickel catalyst, a partially deactivated nickel catalyst, or mixtures thereof. Sulfur-treated catalysts are particularly suitable for use since they promote the rapid development of *trans* isomers during hydrogenation. See, e.g. Okonek, Douglas V., "Nickel-Sulfur Catalysts For Edible Oil Hydrogenation," printed as Chapter 5 of *Hydrogenation: Proceedings of An AOCS Colloquium*, edited by Robert Hastert, 1987.

The hydrogenation catalyst used in the present invention is utilized at a concentration of from about 0.01% to about 0.4%, preferably from about 0.02% to about 0.3%, catalyst by weight of the oil. The amount of catalyst used is dependent upon the rate of reaction to be attained and other variables such as temperature and pressure, and the starting oil.

The time of the total hydrogenation reaction is not critical. The reaction is generally carried out for from about 30 minutes to about 8 hours, and preferably from about 1 hour to about 4 hours. The pressure ranges from about 0

**SUBSTITUTE SHEET**



-7-

psig to about 100 psig, and preferably from about 0 psig to about 80 psig.

The hydrogenation reaction is conducted at a temperature between about 320°F (160°C) and about 500°F (260°C). In order to obtain the frylife improvement benefit of the present invention, during the hydrogenation reaction the temperature of the oil must be between about 440°F (227°C) and about 500°F (260°C) for a time of at least about 5 minutes, and preferably at least about 8 minutes. It is preferred that the oil be held for these times at temperatures between about 460°F (238°C) and about 500°F (260°C), and most preferably between about 470°F (244°C) and about 500°F (260°C).

The method used to control the temperature of the reaction varies with the processing equipment. Since hydrogenation is an exothermic reaction, it may be necessary to cool the reaction by some suitable means, such as a heat exchanger. However, if the vessel is not well insulated or is in a large unheated area, the system may lose heat quickly enough that the heat generated by the exothermic reaction will not be sufficient to maintain the reaction temperature. In this case, it is necessary to apply additional heat by some suitable means, such as heating coils, a heating jacket or heat exchangers.

The reaction is terminated when the iodine value (IV) reaches a value of from about 50 to about 90, and preferably from about 60 to about 80. The endpoint of the reaction is chosen so that the product has the solids content profile desired in that particular product. The solids content can be expressed at different temperatures, in terms of a "Solids Contents Index" (SCI) or "Solid Fat Index" (SFI) which are measured by what is essentially the test described in the Journal of the American Oil Chemists' Society, March 1954, Vol. XXXI, pp. 98-103. The test involves a dilatometric measurement of the amount by which a fat expands when heated from a specific temperature to complete melting.

**SUBSTITUTE SHEET**

-8-

The hydrogenation reaction is generally ended by stopping the flow of hydrogen to the reactor. When the hydrogen flow is stopped, in order to exclude oxygen from the hot oil until it is cooled, generally either the reactor is pressurized with nitrogen or the reactor is kept under a vacuum.

After the hydrogenation reaction is ended, the oil is cooled down from the high temperatures of hydrogenation and stored at a temperature of about 110°F (43°F) to about 220°F (104°C), preferably about 140°F (60°C) to about 180°F (82°C), prior to deodorization. The oil is kept warm enough to avoid the formation of solids, but not too hot because higher temperatures could cause off-flavors and would waste energy.

It is also important after hydrogenation and before deodorization to remove the hydrogenation catalyst by filtering the oil. Further, the oil must be deaerated before it undergoes deodorization, preferably to a level of less than about 0.10% by volume of dissolved oxygen. The order of these processing steps is not critical, but usually the oil is first cooled, then filtered, and then stored, and immediately prior to deodorization the oil is deaerated.

As discussed hereinabove, the fat after hydrogenation has an iodine value (I.V.) of from about 50 to about 90, preferably from about 60 to about 80. The I.V. of a fat or oil indicates the number of grams of Iodine equivalent to halogen absorbed by a 100 gram sample. Because the halogen absorbance is due to the double bonds present in the fatty acid residues attached to the glycerides, the I.V. of a fat or oil can give a general indication of solids content at a given temperature. As the fatty acid residues become more saturated, the fat or oil increases in solids content. In general, the lower the I.V. of a given fat or oil, the greater will be the solids content at a given temperature. The I.V. of a fat or oil can be determined by the AOCS Official Method Col. 1-25, also known as the Wijs method.

**SUBSTITUTE SHEET**

-9-

Approximate iodine values may be determined by measurement of the refractive index of the oil, since for each given oil a linear correlation between iodine value and refractive index can be determined. This method allows a relatively quick and easy determination of the proper endpoint of the hydrogenation.

The content of *trans*-isomers of unsaturated fatty acids in the hydrogenated frying fat of the present invention is measured by infrared spectrometry. The method used is identical to that described by Madison et al. in "Accurate Determination of *Trans* Isomers in Shortening and Oils by Infrared Spectrophotometry," in *J. Amer. Oil Chem. Soc.*, Vol. 59, No. 4 (April, 1982), pp. 178-81, (herein incorporated by reference), with two exceptions: 1) the method utilized in the present invention employed a Nicolet, Model 20DXC, Infrared Spectrometer (Nicolet Instrument Corporation, Madison, WI) which was equipped with a deuterated triglycine-sulfate detector and used in lieu of a Beckman IR012 spectrophotometer; and 2) methyl stearate was replaced with methyl oleate as a calibration standard to be used with methyl elaidate in the construction of the calibration curve.

### 3. Deodorization

The deodorization process used in the present invention is like that described in U.S. patent 4,789,554 to Scavone, et al., issued December 6, 1988, which is incorporated by reference herein. The present deodorization process differs from the Scavone et al. process in that longer deodorization times are permitted. In this deodorization process, the oil is deodorized by heating it at a temperature between about 530°F (277°C) and about 650°F (343°C), at a pressure between about 0.5 mm Hg and about 50 mm Hg, for a time between about 5 seconds and about 35 minutes, while stripping the oil with a stripping medium in the amount of about 0.1% to about 20%

**SUBSTITUTE SHEET**

-10-

by weight of the oil, preferably about 0.5% to about 20%, more preferably about 1% to about 5%.

At col. 3, line 17 to col. 5, line 4 of the above-mentioned Scavone et al. patent, the inventors discuss deep-frying, the undesirable color darkening that occurs in frying fats over time, and the theory behind why the deodorization process works to provide improved frylife. At col. 5, line 5 to col. 7, line 19, Scavone et al. discuss the various stripping factors and their interrelationship in providing a deodorization process that results in optimum frylife of the frying fat.

In any deodorization process, it is important to deaerate the oil before it undergoes deodorization. Scavone et al. discuss a deaeration method at col. 8, line 15 to col. 8, line 37.

After the oil is deaerated, it is deodorized by stripping it with steam or another stripping medium at high temperatures and under vacuum. The temperature can range between 530°F (277°C) and about 650°F (343°C), preferably between about 550°F (288°C) and about 630°F (333°C), and the time of deodorization is between about 5 seconds and about 35 minutes. More preferred times in order of increasing preference are: about 30 seconds to about 30 minutes, about 30 seconds to about 25 minutes, about 30 seconds to about 20 minutes, and about 30 seconds to about 15 minutes. At col. 8, line 38 to col. 9, line 51, the Scavone et al. patent discusses deodorization temperatures, times, pressures and stripping conditions. After the oil is deodorized in a continuous deodorizer, it is rapidly cooled to a temperature below about 480°F (249°C), preferably below about 370°F (188°C), in a short time to avoid an increase in side reactions in the oil. In a semicontinuous deodorizer, the oil is cooled in one or two trays to a temperature of about 150°F (66°C) before leaving the deodorizer.

Any type of deodorization equipment known to the art is suitable for use in the present deodorization process. The

**SUBSTITUTE SHEET**

-11-

Scavone et al. patent describes various types of deodorization equipment and processes at col. 9, line 59 to col. 11, line 28. A continuous deodorizing unit is preferred for use with the invention.

#### 4. Crystallizing and Packaging

The hydrogenated and deodorized frying fat of the present invention can be processed after deodorization by various conventional means well known in the art for processing conventional frying fats, and it can be packaged in any type of suitable container. In general, conventional methods of preparing the frying fat for packaging in cans or similar containers, or for packaging in a bulk cube, involve the steps of (1) heating the frying fat to a temperature (e.g. 39°- 93°C; 100°-200°F) above the melting point of its solid components to form a melt; (2) injecting edible gas such as nitrogen (e.g. 10-25 volume percent) into the melt; (3) passing the melted frying fat through a scraped wall heat exchanger (e.g. to 7°-26.7°C; 45°-80°F), to form a super-cooled mixture containing small crystals; (4) continuing crystallization into the plastic state while mildly agitating in one or more stages; (5) filling into suitable containers; and then, if desired, (6) tempering at a constant temperature (e.g. 27°-32°C; 80°-90°F) while at rest for several hours (e.g. 12-60 hours).

When it is desired to make sheets of frying fat instead of cans or cubes, the processing conditions are changed as follows. First, no nitrogen is injected into the frying fat. Second, crystallization is allowed to take place at rest in a resting tube, instead of being crystallized with agitation. After the resting tube, the fat is extruded onto parchment paper, cut to size, and then packed.

Some methods and apparatus for final processing are described in the following U.S. Patents, all incorporated by reference herein: 2,430,596 to Ziels et al. (assigned to Lever Bros. Co.), issued November 11, 1947; 2,614,937 to

**SUBSTITUTE SHEET**

-12-

Baur et al. (assigned to The Procter & Gamble Co.), issued October 21, 1952; 2,801,177 to Lutton (assigned to The Procter & Gamble Co.), issued July 30, 1957; 3,102,814 to Thompson (assigned to Lever Bros. Co.), issued September 3, 1963; 3,253,927 to Going et al. (assigned to The Procter & Gamble Co.), issued May 31, 1966; and 3,597,230 to Colby et al. (assigned to The Procter & Gamble Co.), issued August 3, 1971.

#### EXAMPLE 1

80,000 pounds of refined and bleached soybean oil having an iodine value of about 130-133 is placed into a batch hardening unit and heated under vacuum to about 330°F (166°C). 50 pounds of a standard nickel catalyst and 50 pounds of a sulfur-poisoned nickel catalyst are added. Hydrogen gas is then bubbled through the batch hardening unit at a pressure of about 50 pounds per square inch-gauge (hereinafter "psig"). The hydrogenation reaction takes place, and the temperature rises to 470°F (243°C). When the iodine value of the product reaches about 71-72, the reaction is ended by stopping the flow of hydrogen, and the product is cooled and then filtered to remove the hydrogenation catalyst. The hydrogenated oil is held at a temperature of 140°-180°F (60°-82°C) prior to deodorization.

The hydrogenated oil is deaerated by placing it into a standard semicontinuous tray deodorizer under a vacuum of less than about 5 mm Hg. The oil is heated to a temperature of about 550°F (288°C). Next the oil is stripped with about 2-3% steam by weight of the oil, for a time of about 20 minutes. Then the deodorization process is stopped and the oil is cooled to about 150°F (66°C) prior to leaving the deodorizer.

The hydrogenated and deodorized oil is lastly pumped through and cooled in a scraped wall heat exchanger and then formed into 5-lb. sheets.

**SUBSTITUTE SHEET**

-13-

The product has the following characteristics:

Iodine value: about 71-72

% *trans*-isomers: about 50%

% saturates: about 21%

Solid fat index: 56% at 50°F (10°C), 43% at 70°F (21°C), 36% at 80°F (27°C), 17% at 92°F (33°C), and 1.5% at 104°F (40°C)

In a more preferred process, the oil of Example 1 hereinabove would be hydrogenated as described hereinabove, and then deodorized in a continuous deodorization apparatus as described in Example 1 of U.S. Patent 4,789,554 to Scavone et al., issued December 6, 1988 (incorporated by reference herein).

#### EXAMPLE 2

##### SAMPLE A

A refined and bleached soybean oil is hydrogenated and deodorized as described in Example 1, with the following changes. 57,000 pounds of oil is placed into a batch hardening unit. The oil is heated under vacuum to 325°F (163°C) instead of 330°F (166°C) before adding the catalyst. During the hydrogenation reaction, the temperature rises to 435°F (224°C) instead of 470°F (243°C). The reaction is ended when the product reaches an iodine value of 71-72. The oil is later pumped through and cooled in a scraped wall heat exchanger and formed into 5-lb. sheets.

The product has the following characteristics:

Iodine value: 71-72

% *trans*-isomers: 48%

% saturates: 22%

Solid fat index: 57% at 50°F (10°C), 44% at 70°F (21°C), 38% at 80°F (27°C), 20% at 92°F (33°C), and 2% at 104°F (40°C).

-14-

SAMPLE B

A refined and bleached soybean oil is hydrogenated as described in Example 1, with the following changes. A 15,000-lb. batch is made instead of an 80,000-lb. batch. 4 lbs. of a standard nickel catalyst is used, and no sulfur-poisoned catalyst is used. The oil is heated to about 300°F (149°C) before it is hydrogenated. During the hydrogenation reaction, the temperature increases to 500°F (260°C). The hydrogenation reaction proceeds until the product reaches an iodine value of about 61. After hydrogenation, the "Sample B" product is blended with liquid soybean oil (iodine value of 107) in a ratio of 78% Sample B to 22% liquid oil. The blend is then deaerated, and then deodorized essentially as described in Example 1 of the Scavone et al. '554 patent, but at a temperature of 600°-605°F (316°-319°C). The blend is later pumped through and cooled in a scraped wall heat exchanger and either formed into 5-lb. sheets or packed into a bulk 50-lb. cube.

The blend has the following characteristics:

Iodine value: about 71

% *trans*-isomers: 31%

% saturates: 29%

Solid fat index: 46% at 50°F (10°C), 39% at 70°F (21°C), 37% at 80°F (27°C), 28% at 92°F (33°C), and 16% at 104°F (40°C).

SAMPLE C

A refined and bleached soybean oil is hydrogenated as described in Example 1, except that a 57,000-lb. batch is made instead of an 80,000-lb. batch. Also, 30 lbs. of a standard nickel catalyst is added when the oil is heated to 270°F (132°C). Then the oil is further heated to 320°F (160°C), and then hydrogenated using a hydrogen pressure of 30 psig. During the hydrogenation reaction, the temperature increases to 450°F (232°C). The reaction is ended when the

**SUBSTITUTE SHEET**



-15-

oil reaches an iodine value of about 60. After hydrogenation, the "Sample C" product is blended in a ratio of 73% Sample C to 27% liquid soybean oil (IV 107). The blend is then deaerated and deodorized as described in Example 1 hereinabove. The blend is later pumped through and cooled in a scraped wall heat exchanger and either formed into 5-lb. sheets or packed into a bulk 50-lb. cube.

The blend has the following characteristics:

Iodine value: about 73

% *trans*-isomers: 36%

% saturates: 27%

Solid fat index: 47% at 50°F (10°C), 40% at 70°F (21°C), 37% at 80°F (27°C), 25% at 92°F (33°C), and 11% at 104°F (40°C).

Frylife Measurements

100% Sample A:

Frylife: 9.24 days\*

Tocopherol: 0.4 mg./g.

% *trans*-isomers: 48%

Hydrogenation temperature (maximum): 435°F (224°C)

-16-

78% Sample B/22% I-107 liquid soybean oil

Frylife: 9.13 days

Tocopherol: 0.17 mg./g.

% *trans*-isomers: 31%

Hydrogenation temperature (maximum): 500°F (260°C)

73% Sample C/27% I-107 liquid soybean oil

Frylife: 8.34 days

Tocopherol: 0.25 mg./g.

% *trans*-isomers: 36%

Hydrogenation temperature (maximum): 450°F (232°C)

- \* The frylife measurement for Sample A is actually 10.99 days. However, Sample A was measured in a different frylife test than Samples B and C, and data shows that the difference in these two tests causes the same oil product to differ from one test to the other by a factor of 1.19. Hence:  $10.99 \text{ days} \div 1.19 = 9.24 \text{ days}$ .

Discussion of Frylife Results

The 73% Sample C/27% I-107 soybean oil mixture has a frylife of 8.34 days, which is not as good as the frylives of the other products. This demonstrates that adding the 27% liquid I-107 soybean oil has a diluting effect on the frylife benefit obtained, even though the liquid oil has undergone a high temperature deodorization process (550°F, 288°C). Accordingly, it is seen that hydrogenating according to the present invention in combination with deodorizing according to the high temperature deodorization conditions of the present invention, produces a better frylife than using high temperature deodorization alone. The best frylife would have occurred if the hydrogenated product had not been diluted with the liquid oil, and if the deodorization step had been conducted at about 600°F (316°C) instead of 550°F (288°C).

Sample A is hydrogenated at 435°F (223°C), whereas Sample B is hydrogenated at 450°F (232°C). A higher

**SUBSTITUTE SHEET**

-17-

hydrogenation temperature as for Sample B improves the frylife. On the other hand, Sample B is diluted 78/22 with the liquid oil, whereas Sample A is not diluted, which would provide Sample A with a frylife advantage. The frylife measurements show that Sample A has a frylife of 9.24 days, while 78% Sample B/22% liquid oil has a similar frylife of 9.13 days. In view of these results, it is believed that the percentage of *trans*-isomers is also having an effect on the frylife. Sample A has a higher *trans*-isomer content of 48% *trans* versus 31% *trans* for the Sample B mixture. This shows that higher *trans*-isomer content may cause an increase in the frylife of a frying oil.

Also, Samples A and C are deodorized at 550°F (288°C), while Sample B is deodorized at 600°F (316°C). One would expect the product deodorized at 600°F (316°C) to have a longer frylife. (Sample B having a longer frylife than Sample C is expected.) Also, Sample A has a higher tocopherol content, which would have been expected to reduce the frylife. That Sample A has about the same frylife as Sample B (9.24 vs. 9.13 days) is attributed to the higher percentage of *trans*-isomers, developed by the high hydrogenation temperature, and to the fact that Sample A was not diluted with the liquid IV-107 oil.

**SUBSTITUTE SHEET**

-18-

CLAIMS

1. A process for making a hydrogenated frying fat with extended frylife comprising:

- a) hydrogenating an edible liquid oil having a starting iodine value between 95 and 150 by reacting the liquid oil with hydrogen in the presence of 0.01% to 0.4% hydrogenation catalyst by weight of the oil, wherein the hydrogenation reaction is conducted at a temperature between 160°C and 260°C and a pressure between 0 psig and 100 psig until the iodine value of the oil after hydrogenation is between 50 and 90, and wherein during the hydrogenation reaction the temperature of the oil is between 227°C and 260°C for a time of at least 5 minutes; then
- b) cooling the oil, filtering the oil to remove the catalyst, storing the oil at a temperature of 43°C to 104°C, and deaerating the oil; and then
- c) deodorizing the oil by heating it at a temperature between 277°C and 343°C, at a pressure between 0.5 mm Hg and 50 mm Hg, for a time between 5 seconds and 35 minutes, while stripping the oil with a stripping medium in the amount of 0.1% to 20% by weight of the oil.

2. A process according to Claim 1 wherein during the hydrogenation reaction the temperature of the oil is between 238°C and 260°C for at least 5 minutes.

3. A process according to Claim 1 wherein during the hydrogenation reaction the temperature of the oil is between 227°C and 260°C for at least 8 minutes.

4. A process for making a hydrogenated frying fat with extended frylife comprising:

**SUBSTITUTE SHEET**

-19-

- a) hydrogenating an edible liquid oil having a starting iodine value between 95 and 150 by reacting the liquid oil with hydrogen in the presence of 0.01% to 0.4% hydrogenation catalyst by weight of the oil, wherein the hydrogenation reaction is conducted at a

temperature between 160°C and 260°C and a pressure between 0 psig and 100 psig until the iodine value of the oil after hydrogenation is between 50 and 90, and wherein during the hydrogenation reaction the temperature of the oil is between 227°C and 260°C for a time sufficient to produce a frying fat containing at least 35% *trans*-isomers; then

- b) cooling the oil, filtering the oil to remove the catalyst, storing the oil at a temperature of 43°C to 104°C, and deaerating the oil; and then
- c) deodorizing the oil by heating it at a temperature between 277°C and 343°C, at a pressure between 0.5 mm Hg and 50 mm Hg, for a time between 5 seconds and 35 minutes, while stripping the oil with a stripping medium in the amount of 0.1% to 20% by weight of the oil.

5. A process according to either of Claims 1 or 4 wherein the hydrogenation catalyst is selected from the group consisting of nickel catalysts, partially deactivated nickel catalysts, and mixtures thereof.

6. A process according to either of Claims 1 or 4 wherein the liquid oil is selected from the group consisting of soybean oil and canola oil, and mixtures thereof.

7. A process according to either of Claims 1 or 4 wherein the oil is deodorized at a temperature between 288°C and 333°C.

8. A process according to either of Claims 1 or 4 wherein the oil is deodorized for a time between 30 seconds and 15 minutes.

**SUBSTITUTE SHEET**

-20-

9. A process according to either of Claims 1 or 4 wherein from 1% to 5% stripping medium is used during the deodorization, and wherein the stripping medium is steam.

10. A process according to either of Claims 1 or 4 wherein during the deodorization the molar ratio of stripping medium to oil is between 0.05 and 9.7, and wherein the combination of stripping parameters is selected so that the stripping factor "f" is greater than about 0.6, where  $f = KP_vS/P_0$ , and wherein "K" is a constant between 1 and 200, " $P_v$ " (the vapor pressure of the component to be stripped) is not more than 0.1 mm Hg at 277°C and not more than 2 mm Hg at 343°C, "S" is the molar steam rate, "P" is the absolute pressure, and "O" is the molar oil rate.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/02685

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (In several classification symbols, indicate any: According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5): A23D 9/00; C11C 3/12 US CL : 426/607; 260/409																	
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched : Classification System : Classification Symbols : US 426/271,417,601,606,607,608,:260/409 Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched :																	
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> : <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of Document, with indication, where appropriate, of the relevant passages : *</th> <th>Relevant to Claim No. : *</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>US, A, 4,229,361 (CAHEN) 21 OCTOBER 1980 See claims 1-6.</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>US, A, 4,260,643 (COCHRAN) 07 APRIL 1981 See column 2, line 5 to column 4, line 58.</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>US, A, 4,567,056 (SCHMIDT) 28 JANUARY 1986 See the abstract and column 2, lines 3-8.</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>US, A, 4,789,554 (SCAVONE) 06 DECEMBER 1988, See the entire patent.</td> <td>1-10</td> </tr> </tbody> </table>			Category *	Citation of Document, with indication, where appropriate, of the relevant passages : *	Relevant to Claim No. : *	Y	US, A, 4,229,361 (CAHEN) 21 OCTOBER 1980 See claims 1-6.	1-10	Y	US, A, 4,260,643 (COCHRAN) 07 APRIL 1981 See column 2, line 5 to column 4, line 58.	1-10	Y	US, A, 4,567,056 (SCHMIDT) 28 JANUARY 1986 See the abstract and column 2, lines 3-8.	1-10	Y	US, A, 4,789,554 (SCAVONE) 06 DECEMBER 1988, See the entire patent.	1-10
Category *	Citation of Document, with indication, where appropriate, of the relevant passages : *	Relevant to Claim No. : *															
Y	US, A, 4,229,361 (CAHEN) 21 OCTOBER 1980 See claims 1-6.	1-10															
Y	US, A, 4,260,643 (COCHRAN) 07 APRIL 1981 See column 2, line 5 to column 4, line 58.	1-10															
Y	US, A, 4,567,056 (SCHMIDT) 28 JANUARY 1986 See the abstract and column 2, lines 3-8.	1-10															
Y	US, A, 4,789,554 (SCAVONE) 06 DECEMBER 1988, See the entire patent.	1-10															
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family																	
<b>IV. CERTIFICATION</b> <table border="1"> <tr> <td>Date of the Actual Completion of the International Search :</td> <td>Date of Mailing of the International Search Report :</td> </tr> <tr> <td>24 MAY 1991</td> <td>27-AUG 1991</td> </tr> <tr> <td>International Searching Authority :</td> <td>Signature of Authorized Officer :</td> </tr> <tr> <td>ISA/US</td> <td>LESLIE WOOD</td> </tr> </table>			Date of the Actual Completion of the International Search :	Date of Mailing of the International Search Report :	24 MAY 1991	27-AUG 1991	International Searching Authority :	Signature of Authorized Officer :	ISA/US	LESLIE WOOD							
Date of the Actual Completion of the International Search :	Date of Mailing of the International Search Report :																
24 MAY 1991	27-AUG 1991																
International Searching Authority :	Signature of Authorized Officer :																
ISA/US	LESLIE WOOD																